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Report Title

Final Report for:

Ln³⁺ Catalyzed Alcoholysis of Organophosphates: New
Methodology for the Catalytic Transformation of Phosphorus Pesticides
and CW Agents

ABSTRACT

The title project involved investigation of the metal ion catalyzed alcoholysis (e.g. methanolysis) of neutral organophosphorus (OP) ester compounds. These included several members of the phosphate [(ArO)(RO)2P=O] and phosphorothioate [(ArS)(RO)2P=O] classes, as well as phosphonate [(ArO)CH3(OR)P=O] and phosphonothioate [(ArS)CH3(RO)P=O] classes. Some work was conducted on the P=S phosphorothionate esters which are common pesticides. In general it was found that La³⁺ ion, in the presence of one equivalent of alkoxide, provided an efficient catalyst capable of decomposing all P=O classes of the above neutral OP agents (except P=S derivatives) at rates between 7 to 9 orders of magnitude larger than the background reactions at the same pH. The Zn(II) and Cu(II) complexes of 1,5,9-triazacyclododecane, as their monoalkoxy forms, are also powerful catalysts for decomposing these OP materials, including the P=S examples. Considerable study was devoted to determining the mechanism of the reactions which is suggested to involve a dual role for the catalyst as both a Lewis acid and deliverer of a metal bound alkoxide to the OP substrate. The metal catalyzed alcoholysis procedures are simple, proceed rapidly at room temperature and essentially neutral pH conditions, give essentially non-toxic ester products from decomposition of the OP simulants investigated.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. R. Stan Brown*, Alexei A. Neverov, Josephine S. W. Tsang, Graham T. T. Gibson and Pedro J. Montoya-Peláez. "Metal Ion Catalyzed Acyl and Phosphoryl Transfer Reactions to Alcohols: La³⁺-Promoted Alcoholysis of Activated Amides, Carboxylate Esters, and Neutral Organophosphorus Esters." Invited Paper for Bader Award Address, Can. J. Chem. 2004, 82, 1791-1805. forms basis of cover for Journal issue
2. J. A. W. Tsang, Alexei A. Neverov and R. S. Brown. "La³⁺-Catalyzed Methanolysis of O,O-Diethyl S-p-nitrophenyl phosphorothioate and O,O-Diethyl S-phenyl phosphorothioate. Millions-fold Acceleration of the Destruction of V-Agent Simulants." Org. Biomol. Chem., 2004, 2, 3457 – 3463.
3. Alexei A. Neverov, N. E. Sunderland and R. Stan. Brown "Metal Ion Promoted Transesterifications of Carboxylate Esters. A Structure/Activity Study of the Efficacy of Zn²⁺ and La³⁺ to Catalyze the Methanolysis of Some Aryl and Aliphatic Esters." Org. Biomol. Chem., 2005, 3, 65 - 72.
4. Tony Liu, Alexei A. Neverov, Josephine S. W. Tsang and R. Stan Brown, "Mechanistic Studies of La³⁺ and Zn²⁺-Catalyzed Methanolysis of Aryl Phosphate and Phosphorothioate Triesters. Development of Artificial Phosphotriesterase Systems." Org. Biomol. Chem. 2005, 3, 1525 – 1533. identified as 'hot article' by the Journal for promotion.
5. Zhong- Lin Lu, Alexei A. Neverov, and R. Stan Brown*, "An Ortho-palladated Dimethylbenzylamine Complex as a Highly Efficient Turnover Catalyst for the Decomposition of P=S Insecticides. Mechanistic Studies of the Methanolysis of Some P=S Containing Phosphorothioate Triesters." Org. Biomol. Chem. 2005, 3, 3379 – 3387. (forms basis for cover of the journal).
6. Roxanne E. Lewis, Alexei A. Neverov and R. S. Brown, "Mechanistic Studies of La³⁺ and Zn²⁺-Catalyzed Methanolysis of O-Ethyl O-aryl methylphosphonate esters. Development of Effective Methods for the Catalytic Destruction of Phosphonate CW Simulants." Org. Biomol. Chem., 2005, 3, 4082 – 4088.
7. Chris Maxwell, Alexei A. Neverov and R. Stan Brown*, "Solvent deuterium kinetic isotope effects for the methanolyses of neutral C=O, P=O and P=S esters catalyzed by triaza:Zn²⁺-methoxide complex." Org. Biomol. Chem. 2005, 3, 4329 – 4336.
8. Stephanie A. Melnychuk, Alexei A. Neverov and R. Stan Brown*, "Rapid decomposition of phosphonothioate esters as simulants for V-agents. Highly efficient catalysis of methanolysis promoted by Zn²⁺- and La³⁺-methoxides." Angewandte Chemie, International Edition 2006, 45, 1767-1770.
9. Graham T. T. Gibson, Mark F. Mohamed, Alexei A. Neverov and R. S. Brown*, "Potentiometric titration of metal ions in ethanol." Inorganic Chemistry, 2006, 45, 7891-7902.

Number of Papers published in peer-reviewed journals: 9.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. June 1, 2004 87th Canadian Chemistry Conference (CSC) and Exhibition, London, Ontario. Bader Award Address by R.S.Brown, "Metal Ion Catalyzed Acyl and Phosphoryl Transfer Reactions to Alcohols: La³⁺-Promoted Alcoholysis of Acetyl Imidazole, Carboxylate Esters, and Neutral Organophosphorus Esters."
 2. Graham Gibson and RSB POMS (Physical Organic Minisymposium) (poster) Nov. 13, 2004 "La³⁺-catalysis of Phosphate Diester Methanolysis: Non-Linear pH-Rate Profiles Aren't So Bad".
 3. CSC – poster by Josephine Tsang, May 28 - June 1, London, Ontario "Mechanism of Methanolyses of Phosphate Triester Derivatives Promoted by La(OTf)₃" -- Josephine S.W. Tsang, Alexei A. Neverov, and R. S. Brown
 4. POMS – talk by Josephine Tsang, Nov 12 - Nov 14, 2004 Kingston, Ontario "Destruction of Chemical Warfare Simulants Catalyzed by La(OTf)₃ in Methanol" -- Josephine S.W. Tsang, Alexei A. Neverov, and R.S. Brown
 5. "Transition Metal Ion-Mediated Decomposition of Oxygen and Sulphur Containing Phosphate Triesters. Billion-fold Acceleration of the Methanolysis of Fenitrothion Promoted by a Simple Cu(II)-Ligand System" A.A. Neverov, Josephine S.W. Tsang and R.S. Brown. Poster "Mechanism of Transition Metal Ion-Mediated Decomposition of Phosphate Triesters."
 6. Billion-fold Acceleration of the Methanolysis of Fenitrothion Promoted by a Simple Cu(II)-Ligand System". A.A. Neverov and R.S. Brown
- 87th Canadian Chemistry Conference and Exhibition, London, Canada, June 2004
7. Poster "Metal Ion Promoted Transesterifications of Carboxylate Esters. A Structure/Activity Study of the Efficacy of Zn²⁺ and La³⁺-Catalyzed Methanolysis of Some Aryl and Aliphatic Esters". A. A. Neverov, N. E. Sunderland and R. S. Brown
- POMS 32, Kingston, Canada, November 2004
8. Invited talk "Metal Ion Catalyzed Alcoholysis Reactions as New Protocols for the Decomposition of Neutral Organo Phosphorus Esters". R. Stan Brown, Alexei A. Neverov, Josephine S. Tsang. DECON 2004, Tampa, Fla, May 2004.
 9. Alexei A. Neverov and R. Stan Brown. Extremely Efficient Lanthanum and Transition Metal Ion-Catalyzed Decomposition of Phosphates and Phosphonates as the model compounds for G- and VX-agents. DECON 2005 12-15 December, Tuscon, Arizona, USA
 10. Alexei A. Neverov, Tony Liu, Roxanne Lewis, Josephine Tsang and R. S. Brown. "The Effect of Leaving group (OAr and SAR) on La³⁺ and Zn²⁺ Catalyzed Methanolysis of Phosphotriesters and MethylPhosphonates" Physical Organic Chemistry Gordon Conference, June, 2005, Plymouth, New Hampshire, USA.
 11. R. Stan Brown, Alexei A. Neverov, Tony Liu, Roxanne Lewis, Stephanie Melnychuk, Chris Maxwell and Josephine S. Tsang. "Mechanistic studies of La³⁺ and Zn²⁺-catalyzed methanolysis of neutral organophosphate esters: concerted reactions of a model for phosphotriesterases." Pacificchem 2005, December 15-20, 2005, Honolulu, invited talk.
 12. May 19-20, 2006, NATO Workshop, Ottawa, Ontario. "La³⁺ and Zn²⁺-catalyzed alcoholysis as a new method for the destruction of CW materials."
 13. September 11-13, 2006, International Chemical Decontamination Workshop for Decontamination of Buildings and Facilities After Chemical Terrorism. Moscow, Russia, "Metal-catalyzed destruction of P-S –containing organophosphates."
 14. Nov 11th POMS Four presentation in poster format by graduate students (Liu, Melnychuk, Mohamed, Maxwell)
 15. DECON 2006, Denver US, Oct 31, Nov 2. United States Army Decontamination Conference. "Use of Solid Supported Mx⁺-catalysts for the Destruction of Neutral Organophosphorus Compounds."

Number of Presentations: 15.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

R. S. Brown and A. A. Neverov, "Metal catalyzed alcoholysis reactions of carboxylate and organophosphorus esters." in "Advances in Physical Organic Chemistry", Vol. 42, J. P. Richard, Ed. Elsevier: Oxford, to be published in 2007

Number of Manuscripts: 1.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Josephine S. W. Tsang	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Benoit Didier	1.00
Zhong-Lin Lu	1.00
Chaomin-Liu	1.00
FTE Equivalent:	3.00
Total Number:	3

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
R. Stan Brown	0.00	No
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Mark Mohamed	0.25
Stephanie Melnychuk	0.25
Roxanne Lewis	0.25
Tony Liu	0.25
Chris Maxwell	0.25
Elizabeth Czaszar	0.25
Kalpa Shah	0.25
FTE Equivalent:	1.75
Total Number:	7

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Josephine S. W. Tsang

Total Number:

1

Names of other research staff

NAME

Alexei A. Neverov

FTE Equivalent:

Total Number:

PERCENT SUPPORTED

1.00 No

1.00

1

Sub Contractors (DD882)

Inventions (DD882)

5 .Method of Decomposing Organophosphorus Compounds

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) Y

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2): European Patent Application

5a: R.Stan Brown

5f-1a: Queen's University

5f-c: 90 Bader Lane

Kingston

On

K7L 3N6

5a: Alexei A. Neverov

5f-1a: Queen's University

5f-c: 90 Bader lane

Kingston

On

K7L 3N6

5a: Josephine S. W. Tsang

5f-1a: Queen's University

5f-c: 90 Bader lane

Kingston

On

K7L 3N6

Final Report for "Ln³⁺ Catalyzed Alcoholysis of Organophosphates: New Methodology for the Catalytic Transformation of Phosphorus Pesticides".

ARO Award W911NF-04-1-0057

March 15, 2005-March 14, 2007

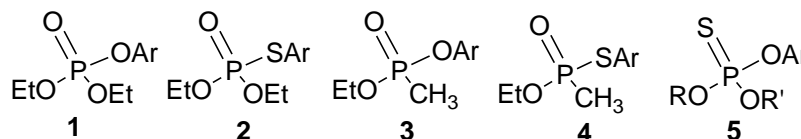
Prepared by: Robert S. Brown

April 14, 2007

Introduction

Over the course of the granting period March 15, 2005 to March 14, 2007 we have performed numerous investigations of the metal ion catalyzed alcoholysis (destruction by reaction with alcohols) reactions of neutral OP compounds which are simulants for the phosphonofluoridate G-agents and phosphonothioate V-agents. In addition, we have investigated systems which catalyzed the alcoholysis of neutral P=S pesticides. This work has lead to nine publications in peer reviewed journals, and at least 15 presentations by me or members of my research group.

The following report is broken into four sections which summarize the work with each of four classes of neutral OP compounds we have investigated; phosphates (**1**) and phosphothioates (**2**), phosphonates (**3**), phosphonothioates (**4**), and phosphothionates (**5**).

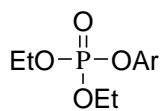


In order to undertake meaningful mechanistic studies in alcohol, it was necessary to understand the determination of pH in these anhydrous solvents, and then to undertake detailed studies of titration of metal containing systems. Fortunately, it is now known that determination of pH in methanol can be easily done through measurements using a calomel electrode similar to how such pH measurements are done in aqueous media¹. In the case of methanol, an electrode is standardized using aqueous buffers, the electrode is then dried with tissue paper, and immersed in the methanol solution, the pH of which is to be determined. After the meter reading is stabilized, a correction factor of 2.24 is added to the meter reading, providing the 'pH' in methanol, herein simply termed pH. In the case of ethanol a similar method is employed, but the correction factor is 2.54². The only other consideration to note is that the autoprotolysis constants differ considerably from that of water (10^{-14}), being respectively $10^{-16.77}$ and $10^{-19.1}$ for methanol and ethanol, meaning that neutral pH in the two solvents is 8.4 and 9.5. As will be seen, all the catalysts we consider for decomposition of the G- and V-agent simulants operate at pH values between 8.2 and 9.5 in methanol, close to neutrality, so the solutions are not caustic or corrosive.

1. Phosphates and phosphothioates

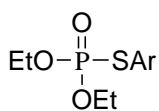
Two series of O-aryl diethyl phosphates and S-aryl diethyl phosphothioates (**1a-g**, **2a-f**) were synthesized and their decomposition in methanol promoted by methoxide,

(La³⁺(⁻OCH₃))₂, and Zn(II)[12]aneN₃ (**6**) was studied at 25 °C using uv/visible spectrophotometry³.



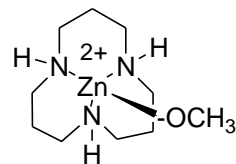
1

- a, Ar = phenyl
- b, Ar = pentafluorophenyl
- c, Ar = 4-chloro-2-nitrophenyl
- d, Ar = 3-nitrophenyl
- e, Ar = 4-chlorophenyl
- f, Ar = 4-methoxyphenyl
- g, Ar = 4-nitro



2

- a, Ar = phenyl
- b, Ar = 4-nitrophenyl
- c, Ar = 4-chlorophenyl
- d, Ar = 3,5-dichlorophenyl
- e, Ar = 4-fluorophenyl
- f, Ar = 4-methoxyphenyl



6

Shown in Figure 1 is a Brønsted plot of the log k_2 vs. pK_a (in methanol) for the reaction of **1** and **2** with methoxide, while Figures 2 and 3 give the Brønsted plots for the reaction of the phosphates (**1**) and phosphorothioates (**2**) with (La³⁺(⁻OCH₃))₂ and **6**.

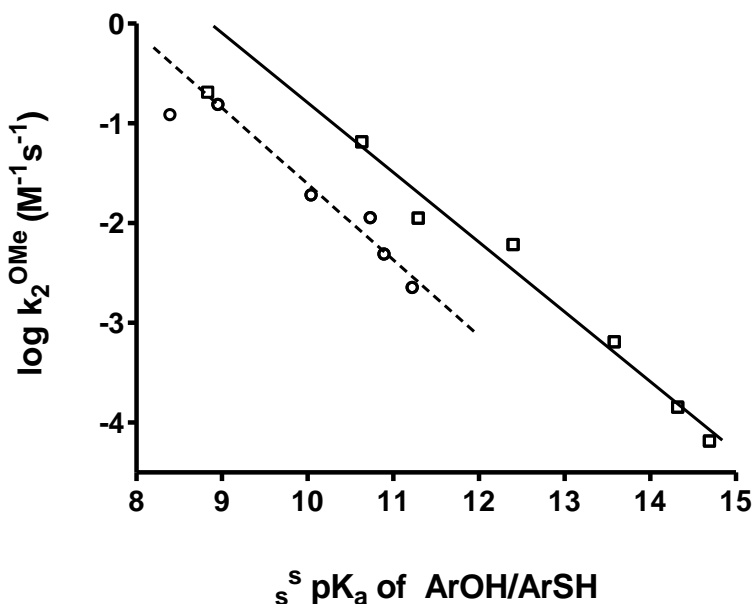


Figure 1. Brønsted plots of the log second order rate constant for methoxide attack on phosphates **1** as well as on phosphorothioates **2** vs. the $s pK_a$ values for the corresponding phenols or thiophenols; linear regressions for the phosphate (except **1b**) and phosphorothioate (except **2b**) data give slopes of -0.70 ± 0.05 (solid line \square) and -0.76 ± 0.08 (dotted line, \circ) respectively.

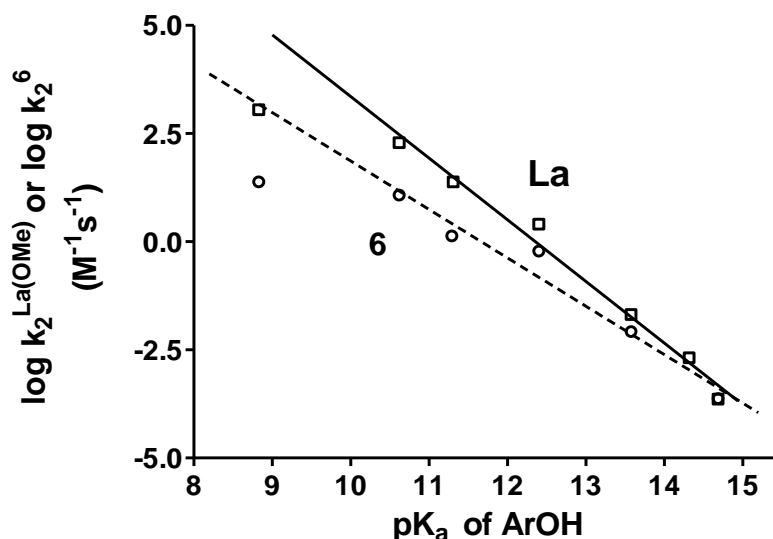


Figure 2. Brønsted plot of the log second order rate constant for La^{3+} - and **6**-catalyzed methanolysis of phosphates **1a-g** vs. the pK_a values for the corresponding phenols; linear regressions through the La^{3+} and **6** data (except **1b**) give gradients of $-(1.43 \pm 0.08)$ (solid line, \square) and $-(1.12 \pm 0.13)$ (dashed line, \circ) respectively. Note points on lower right for the *p*-methoxy derivative (**1f**) are coincident.

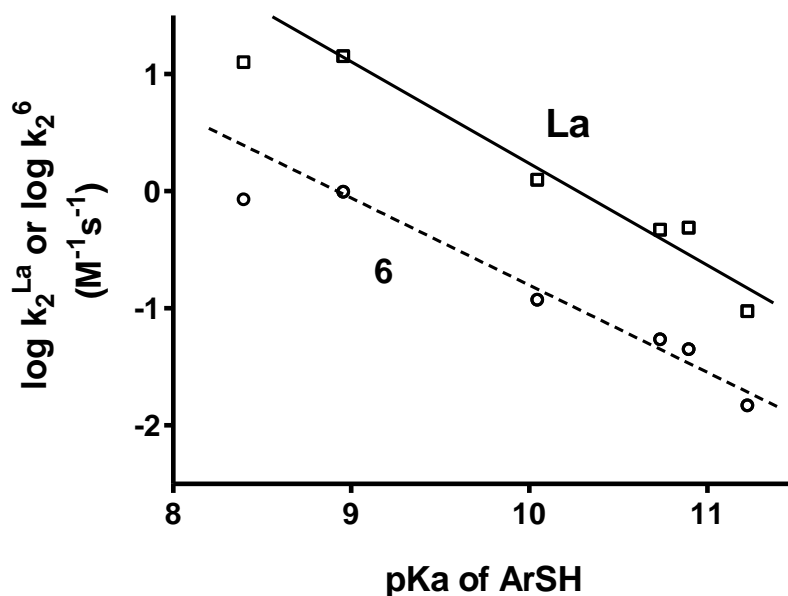
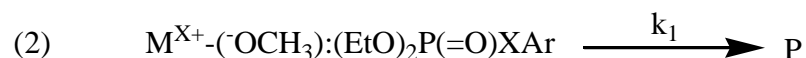
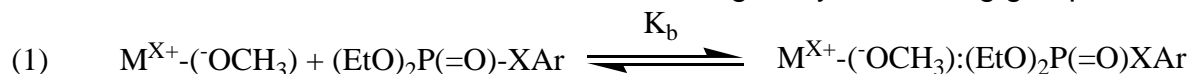
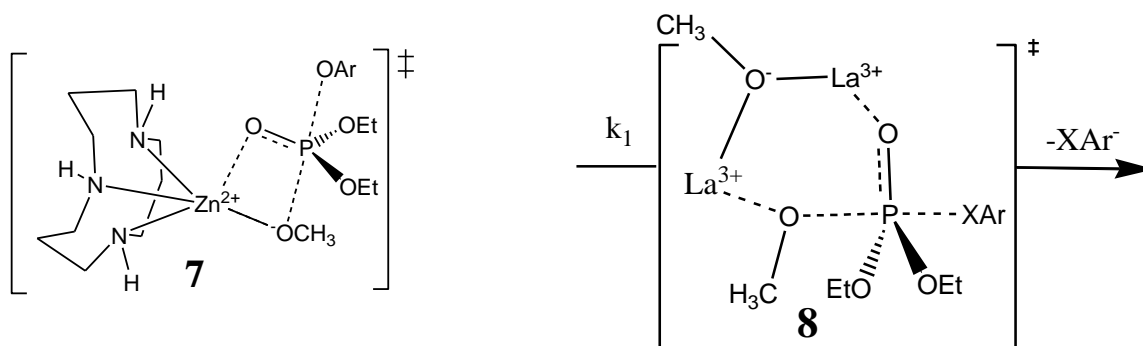


Figure 3. Brønsted plot of the log second order rate constant for La^{3+} - and **6**-catalyzed methanolysis of phosphorothioates **2** vs. the pK_a values for the corresponding thiophenols; linear regressions through the La^{3+} and **6** data give gradients of -0.87 ± 0.10 (solid line, \square) and -0.74 ± 0.06 (dashed line, \circ) respectively.

On the basis of the gradients of the Brønsted plots, several conclusions were made¹. The negative gradient of the line signifies that significant negative charge is building up on the leaving group (O-Ar or S-Ar) in the rate-limiting transition state for the reaction. The general mechanism for the reaction was considered to require two steps, as shown in eq.s (1) and (2), where the first step was a transient binding of the OP compound to the metal-⁻OCH₃ catalyst, followed by a chemical reaction where the metal bound methoxide attacks the P=O unit, driving away the leaving group.



The magnitude of gradient suggested that the reactions, particularly those catalyzed by the metal ions, were probably concerted, proceeding via a hypothetical transition



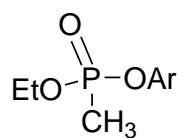
structures **7** and **8**. This sort of concerted transition state is believed to be operative for all the substrates investigated during this project.

It becomes apparent that the catalysis afforded by the La³⁺ and Zn(II) materials from the methanolysis of these phosphates and phosphonates is spectacular. For example, a 1 mM solution of the La³⁺-catalyst is simply prepared from a 2 mM solution of La(O₃SCF₃)₃ in methanol to which has been added 1 equivalent of NaOCH₃ per La³⁺, sets the pH of the solution at ~8.23. The so-formed solution gives an impressive 1.1x10⁹-fold acceleration of the methanolysis of the pesticide paraoxon (**1g**) relative to the background ⁻OCH₃-catalyzed reaction ($k_2^{\text{OCH}_3} = 0.11 \text{ M}^{-1}\text{s}^{-1}$) at that pH⁴. By way of comparison, the background methoxide promoted reaction at pH 8.23 has a t_{1/2} of ~600 years. For the metal catalyzed reactions, the final product is methyl diethyl phosphate which is considered essentially non-toxic (based on the reported toxicity of triethyl phosphate of 1,500 mg/kg, LD₅₀ oral, mouse)

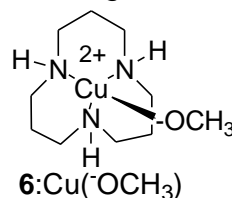
2. Phosphonates

To demonstrate the efficacy of the metal catalyzed alcoholysis for the destruction of G-agents, a series of O-aryl phosphonates (**3a-f**) were prepared and their methanolyses catalyzed by methoxide, (La³⁺(⁻OCH₃))₂ and **5** were studied⁵. Shown in Figure 4 are the Brønsted plots for these reactions in methanol at 25 °C,. Also included

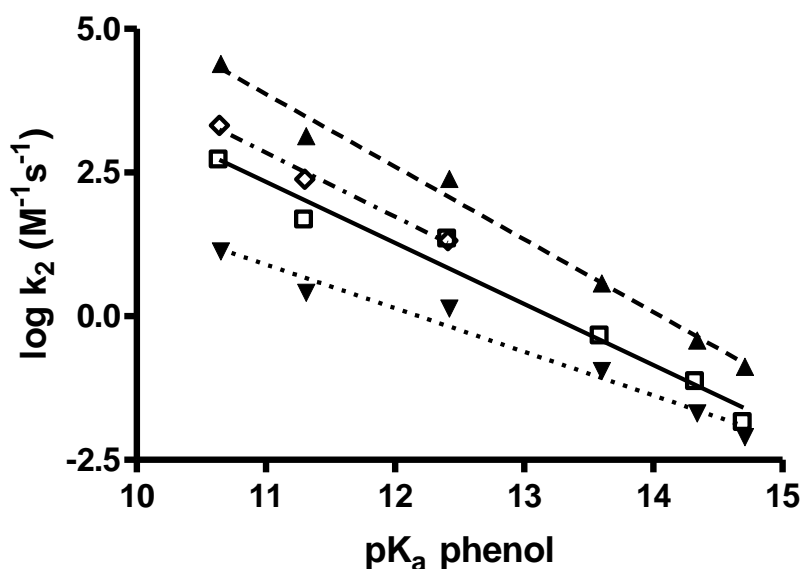
on the plot are data for the Cu^{2+} complex **6**: $\text{Cu}(\text{OCH}_3)$. Once again it is seen that the



- 3** a Ar = (2-NO₂-4-Cl)phenyl
 b Ar = (4-NO₂)phenyl
 c Ar = (3-NO₂)phenyl
 d Ar = (4-Cl)phenyl
 e Ar = phenyl
 f Ar = (4-OCH₃)phenyl



metal catalyzed reactions are much faster than the corresponding methoxide reactions, and the gradients of the plots for these are also steeper (more negative) than for the methoxide reaction. The gradients for the lines are: methoxide (-0.76), $(\text{La}^{3+}_2(\text{OCH}_3))_2$ (-



1.26),

Figure 4. Brønsted plots of the second order rate constants for methoxide and metal ion catalyzed methanolysis of **3a-e** at 25 °C. $(\text{La}^{3+}_2(\text{OCH}_3))_2$ (▲), **6** (□), OCH_3 (▼) and **6**: $\text{Cu}(\text{OCH}_3)$ (◇).

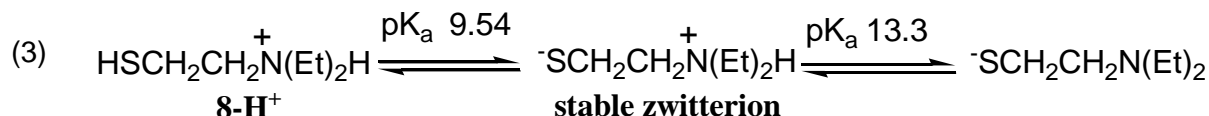
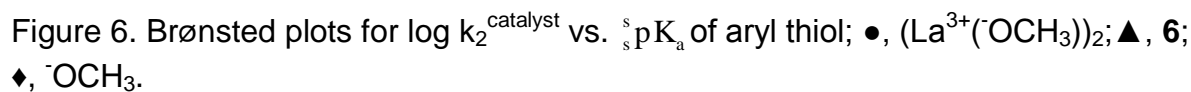
6 (-1.06) and **6**: $\text{Cu}(\text{OCH}_3)$ (-1.12). In the case of the **6**: $\text{Cu}(\text{OCH}_3)$ catalyst, only a limited number of phosphonates could be investigated due to the competing color of the Cu-catalyst which did not allow chromophoric observation of the build-up of the phenols with higher pK_a values.

3. Phosphorothioates.

Our most recent study comprised the La^{3+} and **6**-catalyzed methanolysis of a series of phosphorothioates (**4a-e**) as simulants for the V-agents⁶. Shown in Figure 5 are the Brønsted plots of the methanolysis reaction catalyzed by La^{3+} and **6**. The gradients for the La^{3+} , **6** and OCH_3 lines are -0.75, -0.66 and -0.65, which are within

$$\text{EtO}-\text{P}\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 \end{array}-\text{SAr}$$

4a Ar=3,5-dichlorophenyl
 b Ar = 4-chlorophenyl
 c Ar = 4-fluorophenyl
 d Ar = phenyl
 e Ar = 4-methoxyphenyl



the amino group would be substantially protonated at that pH, and so the appropriate pK_a would be the one for formation of the stable zwitterion (9.54). This is identified on the plots shown in Figure 6 as a vertical dotted line. From the linear regression lines for the La^{3+} and **6** reactions, one can determine the predicted $k_2^{catalyst}$ values which suggest that a solution containing **6** or $(La^{3+}(\bar{O}CH_3))_2$ should methanolyze V-X with respective $t_{1/2}$ values of 18 and 0.33 sec. at ambient temperature and essentially neutral conditions, the phosphorus-containing product being ethyl methyl methylphosphonate.

4. Summary

From the above and the additional peer-reviewed publications documented in the Final Report for ARO Award W911NF-04-1-0057, it can be seen that metal catalyzed alcoholysis reactions prove to be particularly effective for the catalytic decomposition of neutral OP esters that can be considered to be simulants of G- and V-agents. The reactions are simple to perform, do not require specialized equipment, work at ambient temperature and below under essentially neutral pH conditions, and produce products which are considered to be non-toxic. Additional work might be performed to attach the catalytic systems to solid supports such as polymers or silicates to produce immobilized catalysts that could be reused. In this form, one might make a material that can be used for the decontamination of sensitive equipment where the contaminant is removed by alcohol dissolution, and the solution is passed through a column containing the catalytic material.

Cited references.

1. Graham Gibson, Alexei A. Neverov and R. S. Brown " Potentiometric Titrations of Metal Ions in Methanol" *Can. J. Chem.* **2003**, 81, 495-504.
2. Graham T. T. Gibson, Mark F. Mohamed, Alexei A. Neverov and R. S. Brown*, "Potentiometric titration of metal ions in ethanol." *Inorganic Chemistry*, **2006**, 45, 7891-7902.
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